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DFT Approach to the Calculation of Mössbauer Isomer Shifts

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Abstract: With the help of a recently suggested computational scheme [*J. Chem. Phys.* **2007**, *127*, 084101], Mössbauer isomer shifts are calculated within the context of density functional theory, for a series of iron containing compounds. The influence of the choice of a density functional and of the truncation of a basis set on the results of calculations is analyzed. It has been observed that the hybrid density functionals, especially BH&HLYP, provide better correlation with experimental results than pure density functionals. The analysis of basis set truncation reveals that the addition (or removal) of the tightmost primitive functions to a large uncontracted basis set has only a minor influence on the calculated isomer shift values. It is observed that, with the use of a small contracted basis set, a reasonable accuracy for the calculated isomer shifts can be achieved.

I. Introduction

Mössbauer spectroscopy[1] is a powerful analytic tool which enables one to obtain valuable information about the geometric and electronic structure of chemical compounds.[2−7] The method is based on the Mössbauer effect[1] which is the recoil emission/absorption of γ radiation from a solid sample.[2−4] The most well-known application of Mössbauer spectroscopy is for the determination of ^{57}Fe in metal complexes. However, there exist more than 40 other elements in the periodic table which possess γ-active isotopes and for which the Mössbauer spectra can be obtained.[2−5] Due to the high sensitivity of the method and its independence on the perfect crystalline structure of the samples, Mössbauer spectroscopy finds an ever increasing number of applications which range from biological chemistry[6] and nanotechnology[7] to materials science.[4]

One of the most important characteristics of the Mössbauer spectrum is the so-called Mössbauer isomer shift (MIS).[8] MIS is the measure of the energy difference between the γ-transitions in the source (E_s) and the absorber (E_a) nuclei. Commonly MIS, δ in eq 1, is measured in terms of the Doppler velocity necessary to achieve resonance absorption of γ-radiation.

$$\delta = \frac{c}{E_\gamma}(E_a - E_s) \tag{1}$$

Within the standard approach to the Mössbauer effect,[2,3,10−16] the MIS is connected to the electron density at the nucleus via eq 2

$$\delta = \frac{c}{E_\gamma}\frac{4\pi}{5} ZS(Z)R^2\left(\frac{\Delta R}{R}\right)(\bar{\rho}_e^a - \bar{\rho}_e^s) \tag{2}$$

where E_γ is the energy of the nuclear γ-transition, c is the velocity of light, Z and R are the nuclear charge and radius, ΔR is the variation of the nuclear radius, and $\bar{\rho}_e^a$ and $\bar{\rho}_e^s$ are the average electronic densities inside the absorber and the source nucleus, respectively.

According to eq 2, it is the variation of nuclear volume during Mössbauer γ-transition that is responsible for the occurrence of MIS.[2,3,9] This equation is most straightforwardly derived within the nonrelativistic formalism. Within this formalism, the electron density remains finite in the vicinity of a point-charge nucleus. With the use of relativistic formalism, the density is divergent at the nuclear position. It is therefore necessary to carry out averaging of the electron density within a sphere of finite radius, which represents nuclear volume.[3,17] The use of the density at the nuclear position, obtained in relativistic calculations with point-

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charge nucleus, may lead to large errors which manifest in unrealistic contact densities. However, in finite basis set calculations, such errors are difficult to detect especially if the basis set does not contain sufficiently tight basis functions.[18]

Most commonly, the contact density obtained in nonrelativistic calculations is corrected for relativistic effects with the use of a scaling factor $S(Z)$ in eq 2.[2,3,9−11] The contact density can be straightforwardly obtained with the use of a method based on the variational principle, such as the self-consistent field method, the variational configuration interaction, or the Kohn−Sham method. However, with the use of methods based on the perturbation theory, the so-called relaxed density matrix needs to be calculated,[19] which presently is not routinely available for multireference many-body perturbation theory methods.

It is a common practice within the standard approach to the calculation of MIS to treat the factor in front of the density difference in eq 2 as an empirical parameter, the value of which is determined from the fit of the theoretically calculated densities versus the experimentally observed isomer shifts.[12−16] The so-obtained parameters of nuclear transitions may differ by a factor of 2 from the experimentally obtained values.[3]

Recently, a new approach[20] to the calculation of MIS was suggested. Within this approach, the energy shift of the nuclear γ-transition is expressed in terms of the derivative of the electronic energy with respect to the radius of a finite nucleus. This approach incorporates inherently the effects of relativity and electron correlation. According to the new approach, the MIS is calculated as in eq 3

$$\delta = \frac{c}{E_\gamma}\left(\frac{\delta E_e^a(R_N)}{\delta R_\mathrm{N}}\bigg|_{R_{N=R}} - \frac{\delta E_e^s(R_N)}{\delta R_\mathrm{N}}\bigg|_{R_{N=R}}\right)\Delta R \qquad (3)$$

where E_e^a and E_e^s are the electronic energies of systems containing the absorber and the source nuclei. In the calculations with eq 3,[20] the experimental values of the parameters of nuclear transitions, ΔR and E_γ, were employed which were taken from the compilation in ref 3, and the experimental values of the nuclear radii R were taken from ref 21.

The new method for the calculation of Mössbauer isomer shifts (MIS) has been initially tested in the calculations which employed large uncontracted basis sets and a series of wave function methods ranging from the HF method to the CCSD-(T) method.[20] The calculations have been carried out for a number of atoms and a series of iron clusters. The major idea underlying these benchmark calculations was to demonstrate the applicability of the new approach to the calculation of MIS and to demonstrate that the use of empirically adjusted parameters can be avoided with the use of the new method.[20]

However, several questions remained open in the initial study. In particular, the dependence of the results on the basis set truncation was not addressed. Furthermore, the use of the advanced wave function methods may be prohibitively costly for calculations on large biological systems or on cluster models of solids. The methods based on density functional theory are more preferable in this respect. Therefore, in the present work, we would like to address two issues: i) sensitivity of the results to the choice of the basis set and ii) utility of density functional methods for the calculation of MIS within the new approach.

II. Computational Details

All calculations were carried out using the COLOGNE 2005[22] suite of programs in which the new computational scheme is implemented. The relativistic calculations were carried out within one-electron approximation[23] and using the normalized elimination of the small component (NESC)[24] method which was implemented according to ref 25. The nonrelativistic calculations were carried out within the same formalism by setting a high value (10^8 au) for the velocity of light.

The Density Functional Theory methods used here are PBE[26] (gradient-corrected correlation functional of Perdew, Burke, and Ernzerhof), BPW91 (Becke 88 exchange[27] and Perdew−Wang 91 correlation functionals[28]), BLYP (Becke 88 exchange and LYP[29] correlation functional), B3LYP[30] (Becke Three Parameter Hybrid Functionals with LYP correlation functional), and BH&HLYP (B stands for Becke treatment of the exchange functional, H&H means half Hartree−Fock exchange and half Slater exchange,[31] the correlation part being the LYP functional). The basis sets employed will be specified in the following section.

Throughout this work the Gaussian nucleus model[21,32] is used in the calculations. The derivatives in eq 3, $(\delta E_e^a(R_N))/(\delta R_N)$, are calculated numerically using the increment of 10^{-6} au for the rms nuclear radius. The use of numeric differentiation helps to avoid the difficulties with obtaining the energy derivatives within the computational schemes for which the Hellmann−Feynman theorem is not satisfied.

When calculating the isomer shifts, the effective electron density inside the nucleus was first calculated using eq 4.[20]

$$\bar{\rho}_e = \frac{5}{4\pi ZR}\frac{\delta E_e^a(R_N)}{\delta R_\mathrm{N}}|_{R_{N=R}} \qquad (4)$$

Then the isomer shifts were calculated from eq 5, where the proportionality constant ($a = -0.1573 a_0^3$ mm s^{-1}) is determined from the experimental parameters of the ^{57}Fe nuclear transitions reported in ref 3.

$$\delta = a(\bar{\rho}_e^a - \bar{\rho}_e^s) \qquad (5)$$

Note that this value differs by a factor of more than 2 from the proportionality constants calibrated by an empirical fit of the calculated electron densities versus the observed isomer shifts (see, e.g., refs 12−16).

III. Results and Discussion

In the present work, the MIS calculations are carried out for the following series of iron clusters: $[Fe(H_2O)_6]^{2+}$, $[FeCl_4]^{2-}$, $[Fe(H_2O)_6]^{3+}$, $[FeF_6]^{3-}$, $[FeI_4]^{1-}$, $[FeBr_4]^{-1}$, $[FeCl_4]^{-1}$, $[Fe(CN)_6]^{3-}$, $[Fe(CO)_5]$, $[Fe(CO)_4]^{2-}$, $[Fe(CN)_5NO]^{2-}$, and $[FeO_4]^{2-}$. The geometries were taken from the compilation in refs 2 and 12 and from ref 33 ($Fe(CO)_5$). The MIS values

Table 1. HF Calculations of Mossbauer Isomer Shifts for Different Iron Containing Clusters by Using Relativistic and Nonrelativistic Methods[c]

	exptl	ref[a]	24s15p9d3f	23s15p9d3f	22s15p9d3f	21s15p9d3f	20s15p9d3f
1 $[Fe(H_2O)_6]^{2+}$	1.41	12	0.89(0.63)[b]	0.81(0.63)	0.83 (0.63)	0.81(0.63)	0.79(0.63)
2 $[FeCl_4]^{2-}$	0.92	12	0.65(0.35)	0.65(0.35)	0.67(0.37)	0.66(0.37)	0.65(0.37)
3 $[Fe(H_2O)_6]^{3+}$	0.52	12	0.22(0.16)	0.22(0.16)	0.22(0.16)	0.22(0.16)	0.21(0.15)
4 $[FeF_6]^{3-}$	0.50	12	0.26(0.19)	0.26(0.19)	0.26 (0.19)	0.26(0.19)	0.24 (0.19)
6 $[FeBr_4]^{1-}$	0.29	42	0.10(−0.03)	0.08(−0.03)	0.08 (−0.03)	0.04(−0.03)	−0.02(−0.03)
7 $[FeCl_4]^{1-}$	0.22	42	−0.02(−0.02)	−0.02(−0.02)	−0.02(−0.02)	−0.02(−0.02)	−0.02(−0.02)
8 $[Fe(CN)_6]^{3-}$	−0.11	12	−0.20(−0.17)	−0.21(−0.17)	−0.22(−0.17)	−0.20(−0.10)	−0.22(−0.17)
9 $[Fe(CO)_5]$	−0.12	33	−0.09(−0.07)	−0.09(−0.07)	−0.09(−0.07)	−0.09(−0.07)	−0.10(−0.07)
10 $[Fe(CO)_4]^{2-}$	−0.12	33	0.07(0.06)	0.05(0.06)	0.05(0.06)	0.03(0.04)	0.03(0.04)
12 $[FeO_4]^{2-}$	−0.67	43	−0.99 (−0.77)	−0.99(−0.77)	−0.99(−0.77)	−0.99(−0.77)	−0.97 (−0.77)

[a] Sources of experimental values. [b] In parentheses, the results of nonrelativistic calculations. [c] All shifts are given with respect to $[Fe(CN)_6]^{4-}$ ($\delta = -0.02$). See refs 12, 14, and 20.

Table 2. DFT Calculations (PBE) of Mossbauer Isomer Shifts for Different Iron Containing Clusters by Using Relativistic and Nonrelativistic Methods[b]

	exptl	24s15p9d3f	23s15p9d3f	22s15p9d3f	21s15p9d3f	20s15p9d3f
1 $[Fe(H_2O)_6]^{2+}$	1.41	0.70(0.54)[a]	0.70(0.54)	0.58(0.54)	0.69(0.54)	0.67(0.54)
2 $[FeCl_4]^{2-}$	0.92	0.37(0.29)	0.37(0.29)	0.38(0.30)	0.38(0.30)	0.38(0.30)
3 $[Fe(H_2O)_6]^{3+}$	0.52	0.34 (0.27)	0.34 (0.27)	0.34(0.27)	0.34(0.27)	0.33 (0.27)
4 $[FeF_6]^{3-}$	0.50	0.34(0.26)	0.34(0.26)	0.33 (0.22)	0.32(0.26)	0.33(0.26)
6 $[FeBr_4]^{1-}$	0.29	n.a.(0.20)	n.a.(0.20)	n.a.(0.20)	n.a.(0.20)	0.14(0.20)
7 $[FeCl_4]^{1-}$	0.22	0.21(0.17)	0.19(0.17)	0.21(0.17)	0.20(0.17)	0.20(0.17)
8 $[Fe(CN)_6]^{3-}$	−0.11	−0.06(−0.05)	−0.06(−0.05)	−0.04(−0.04)	0.01(−0.05)	−0.06(−0.05)
9 $[Fe(CO)_5]$	−0.12	−0.02(−0.03)	−0.02(−0.03)	−0.02(−0.03)	−0.02(−0.03)	−0.02(−0.02)
10 $[Fe(CO)_4]^{2-}$	−0.12	0.07(0.06)	0.07(0.06)	0.07(0.06)	0.06(0.05)	0.06(0.06)
12 $[FeO_4]^{2-}$	−0.67	−0.40(−0.31)	−0.41(−0.31)	−0.40(−0.31)	−0.41(−0.31)	−0.39(−0.31)

[a] In parentheses, the results of nonrelativistic calculations. [b] All shifts are given with respect to $[Fe(CN)_6]^{4-}$.

for these compounds range from a large positive value of +1.48 mm/s for $[Fe(H_2O)_6]^{2+}$ to −0.69 mm/s for $[FeO_4]^{2-}$. The sources of experimental values for each of these clusters are reported in Table 1.

First we would like to address the question of the basis set dependence of the MIS calculated according to eqs 3−5.

A. Influence of Basis Sets on Isomer Shift Values. In the preliminary study, reported in ref 20, the large uncontracted basis sets for iron complexes were employed. These basis sets were constructed by augmenting the standard (20s12p9d) Fe basis set of Partridge[34] with four tight primitive s-type Gaussian functions and with a set of polarization functions taken from the TZVpp basis set of Ahlrichs and May.[35] The so-obtained (24s15p9d3f) basis set for iron was combined with the uncontracted aug-cc-pVDZ basis set of Dunning[36] on other atoms with the only exception of iodine for which the 6-311G* basis set[37] was used.

In the present work, we carry out calculations with this basis set (denoted further on as basis set A+) for a truncated set of compounds (see Tables 1 and 2) to make a connection to the previous work with this method.[20] In the calculations carried out at the Hartree−Fock and PBE density functional levels of theory, we study the effect of truncation of the tight primitive basis functions on the theoretical MISs. The results of the calculations are reported in Tables 1 (Hartree−Fock) and 2 (PBE density functional).

Analysis of the HF results suggests that the MIS calculated with eqs 3−5 are not very sensitive to the truncation of tight primitive basis functions. In most cases, there is only a modest variation (ca. 10%) in the MIS obtained at the relativistic level of theory. The only marked exception is the iron bromide cluster (see entry 6 in the tables), for which the use of truncated basis sets leads to a certain deterioration of the results obtained with the inclusion of relativity. The nonrelativistic HF results obtained with eqs 3−5 do not show any noticeable dependence on the truncation of the basis set.

The same trends, a weak dependence of the relativistic results and an independence of the nonrelativistic results on the basis set truncation, is observed in the density functional calculations (see Table 2). In most cases, the variation in the calculated MIS is of the order of 10% or less. The use of a basis set augmented with tight s-type primitives led, in the case of relativistic density functional calculations for iron bromide (as well as iodide), to serious convergence problems. The source of these problems is most likely in the use of the numeric quadratures inappropriate for relativistic calculations with tight functions. In the nonrelativistic calculations with eqs 3−5, no convergence problems were observed with the use of the very tight functions in the basis sets.

The results reported in Tables 1 and 2 suggest that the converged theoretical results can be obtained with the use of the (21s15p9d3f) iron basis set which is augmented with only one tight primitive function. This basis set (denoted further on as basis set A) will be used in further study of the accuracy of different density functional methods. This basis set is however too big to be used in practical calculations on large molecular systems. The use of standard basis sets, such as the (14s11p6d3f)/[8s7p4d1f] basis set of

Table 3. Comparison of DFT, HF, and MP2 Results for Basis Sets A+ and B[e]

		A[a]			B[b]		
	exptl	PBE	HF	MP2	PBE	HF	MP2
1 $[Fe(H_2O)_6]^{2+}$	1.41	0.70	0.89	0.96	0.62	0.72	0.82
2 $[FeCl_4]^{2-}$	0.92	0.38	0.66	0.56	0.35	0.36	0.49
3 $[Fe(H_2O)_6]^{3+}$	0.52	0.34	0.22	0.37	0.32	0.21	0.32
4 $[FeF_6]^{3-}$	0.50	0.34	0.26	0.41	0.31	0.25	0.35
5 $[FeI_4]^{1-}$	0.31[c]	n.a.	0.04	0.30	0.48	0.02	0.19
6 $[FeBr_4]^{1-}$	0.29	n.a.	0.10	0.32	0.21	0.00	0.19
7 $[FeCl_4]^{1-}$	0.22	0.21	−0.02	0.18	0.20	0.002	0.17
8 $[Fe(CN)_6]^{3-}$	−0.11	−0.06	−0.20	0.05	−0.05	−0.18	0.04
9 $[Fe(CO)_5]$	−0.12	−0.02	−0.09	0.00	−0.02	−0.07	0.02
10 $[Fe(CO)_4]^{2-}$	−0.12	0.06	0.03	0.05	0.07	0.01	−0.26
11 $[Fe(CN)_5NO]^{2-}$	−0.12[d]	n.a.	−0.23	−0.17	n.a.	−0.16	0.02
12 $[FeO_4]^{2-}$	−0.67	−0.40	−0.99	−0.31	−0.32	−0.82	0.04

[a] By using basis set A+. [b] By using basis set B. [c] Reference 42. [d] Reference 5. [e] See text for details of basis sets.

Wachters[38] (Fe) and the 6-31+G* Pople's basis set[39] on nonmetal atoms, is a common practice in the calculations on large metal complexes.[13] This basis set is denoted further on as basis set B. In the current work we employed the DZVP basis set[40] on iodine.

Table 3 reports the results of MIS calculations carried out at the Hartree−Fock, MP2, and DFT (PBE) levels of theory with the use of the basis set B. These results are compared with the results of the calculations carried out with the use of the large A+ basis set. The results obtained with the density functional method are surprisingly stable with respect to the replacement of the large uncontracted basis set A+ with a standard contracted basis B. The greatest difference (ca. 20%) is for the iron tetroxide cluster which may require an extended basis set for the correct description of the ligand back-donation effects. Note however that the effect of relativity is less visible with the use of a small basis set B. This is understandable, because this basis set does not contain tight basis functions needed to describe the relativistic contraction of the electron density.

The HF results in Table 3 are even less sensitive than DFT to the replacement of the uncontracted basis set with the standard contracted basis set. However, the MP2 results show much greater sensitivity to the basis set truncation. The greatest discrepancy is observed for the iron tetroxide cluster (entry 12), which indicates that the proper description of its electronic structure cannot be achieved with the use of the small basis set at the MP2 level.

To summarize this subsection, the calculations of MIS carried out with the use of different basis sets suggest that reasonable results can be obtained at the Hartree−Fock or at the density functional levels of theory with the use of standard contracted basis sets. However, the use of small basis sets in connection with the MP2 method leads to a considerable deterioration of the results for certain compounds. This suggests that extended basis sets, such as the basis sets A or A+, need to be used in connection with MP2.

B. Isomer Shift Variation with Different Theoretical Levels. The results reported in Table 3 show that the inclusion of electron correlation via density functionals has a noticeable effect on the calculated MIS. In almost all cases, there is an improvement in the calculated isomer shifts as compared to the HF values. Noticeable improvement is obtained for iron halides, cyanides, and oxide clusters. The magnitude of the improvement is comparable with the improvement brought about by MP2 for the large basis set A. For the standard contracted basis set B, the PBE results are noticeably better than the MP2 results with one exception of the Fe(II) aqua complex.

In this subsection, we undertake a study of the dependence of the calculated MIS on the choice of the density functional employed. For this study, we select several popular density functionals: PBE, BPW91, BLYP, B3LYP, and BH&HLYP. In this selection of functionals, there are two series which characterize i) the dependence of the results on specific parametrization of a pure exchange-correlation density functional (series PBE, BPW91, BLYP) and ii) the dependence of the results on the use of varying fraction of the HF exchange in a hybrid HF/DFT functional (series BLYP, B3LYP, BH&HLYP). In our opinion, this selection of functionals enables one to make a reasonable judgment on the performance of different types of density functionals.

The criteria employed to judge the performance of density functionals in the MIS calculations with eqs 3−5 are as follows: a) The mean absolute error which is a characteristic commonly employed to judge the overall performance of computational schemes. b) The slope and the intercept of a least-squares linear fit of the experimental vs calculated isomer shifts, eq 6.

$$\delta^{exp} = \alpha.\delta^{calc} + \beta \tag{6}$$

The latter two parameters characterize the correlation of the calculated MIS with the experimental values (slope of the linear fit, α) and the systematic error in the calculated MIS (the intercept of the linear fit, β).

The results of the density functional and HF calculations are summarized in Tables 4 (basis set A) and 5 (basis set B). Notably the choice of the parametrization of a pure density functional has a negligible effect on the calculated MIS regardless of whether a large (A) or a small (B) basis set is employed. The mean absolute error and the parameters of the linear fit remain nearly the same for different pure density functionals. This observation suggests that it is sufficient to study the effect of hybridization with varying

Table 4. Calculation of Mossbauer Isomer Shifts (mm/s) for Different Iron Containing Clusters by Using Basis Set A[d]

	exptl	PBE	BPW91	BLYP	B3LYP	BH&HLYP	HF
1 $[Fe(H_2O)_6]^{2+}$	1.41	0.69(0.54)[a]	0.69(0.54)	0.67(0.52)	0.71(0.56)	0.77(0.60)	0.81(0.63)
2 $[FeCl_4]^{2-}$	0.92	0.38(0.30)	0.38(0.30)	0.37(0.29)	0.39(0.31)	0.43(0.34)	0.66(0.37)
3 $[Fe(H_2O)_6]^{3+}$	0.52	0.34(0.27)	0.32(0.26)	0.32(0.25)	0.28(0.22)	0.24(0.18)	0.22(0.16)
4 $[FeF_6]^{3-}$	0.50	0.32(0.26)	0.32(0.26)	0.32(0.25)	0.30(0.23)	0.28(0.21)	0.26(0.19)
5 $[FeI_4]^{1-}$	0.31	n.a.	n.a.	n.a.	n.a.	n.a.	0.09(0.07)
6 $[FeBr_4]^{1-}$	0.29	n.a.	n.a.	n.a.	n.a	n.a.	0.04(−0.03)
7 $[FeCl_4]^{1-}$	0.22	0.20(0.17)	0.20(0.34)	0.39(0.33)	0.32(0.29)	0.24(0.23)	−0.02(−0.02)
8 $[Fe(CN)_6]^{3-}$	−0.11	0.01(−0.05)	−0.06(−0.05)	0.02(−0.05)	0.00(−0.06)	−0.04(−0.02)	−0.20(−0.10)
9 $[Fe(CO)_5]$	−0.12	−0.02(−0.03)	−0.02(−0.03)	−0.03(−0.03)	−0.04(−0.03)	−0.05(−0.04)	−0.09(−0.07)
10 $[Fe(CO)_4]^{2-}$	−0.12	0.06(0.05)	0.06(0.05)	0.06(0.05)	0.05(0.04)	0.01(0.02)	0.03(0.04)
11 $[Fe(CN)_5NO]^{2-}$	−0.12	n.a.[b]	n.a.	n.a.	−0.20(−0.16)	−0.28(−0.22)	−0.19(−0.10)
12 $[FeO_4]^{2-}$	−0.67	−0.41(−0.31)	−0.41(−0.32)	−0.41(−0.32)	−0.51(−0.40)	−0.63(−0.49)	−0.99(−0.77)
MAE[c]		0.26(0.30)	0.25(0.31)	0.28(0.31)	0.24(0.28)	0.21(0.26)	0.23(0.26)
slope		0.48(0.38)	0.49(0.38)	0.46(0.37)	0.53(0.43)	0.61(0.47)	0.78(0.56)
intercept		0.04(0.02)	0.03(0.04)	0.06(0.04)	0.00(0.00)	−0.05(−0.03)	−0.14(−0.11)

[α] In parentheses, the results of nonrelativistic calculations. [b] The results are not available due to poor SCF convergence in the broken-symmetry spin unrestricted method. [c] Mean absolute error of the method. [d] See text for details of basis set. All shifts are given with respect to $[Fe(CN)_6]^{4-}$.

Table 5. Calculation of Mossbauer Isomer Shifts (mm/s) for Different Iron Containing Clusters by Using Basis Set B[d]

	exptl	PBE	BPW91	BLYP	B3LYP	BH&HLYP	HF
1 $[Fe(H_2O)_6]^{2+}$	1.41	0.62(0.53)[a]	0.62(0.57)	0.60(0.55)	0.61(0.55)	0.65(0.59)	0.72(0.65)
2 $[FeCl_4]^{2-}$	0.92	0.35(0.29)	0.35(0.32)	0.34(0.31)	0.33(0.30)	0.34(0.32)	0.36(0.30)
3 $[Fe(H_2O)_6]^{3+}$	0.52	0.32(0.26)	0.31(0.28)	0.30(0.28)	0.24(0.21)	0.23(0.17)	0.21(0.17)
4 $[FeF_6]^{3-}$	0.50	0.31(0.25)	0.31(0.28)	0.30(0.28)	0.26(0.22)	0.23(0.19)	0.25(0.20)
5 $[FeI_4]^{1-}$	0.31	0.48(0.47)	0.48(0.47)	0.47(0.48)	0.16(0.16)	0.11(0.10)	0.02(0.05)
6 $[FeBr_4]^{1-}$	0.29	0.21(0.19)	0.23(0.23)	0.22(0.21)	0.15(0.14)	0.07(0.07)	0.00(0.00)
7 $[FeCl_4]^{1-}$	0.22	0.20(0.16)	0.20(0.18)	0.19(0.18)	0.13(0.11)	0.06(0.05)	0.00(−0.01)
8 $[Fe(CN)_6]^{3-}$	−0.11	−0.05(−0.08)	−0.05(−0.05)	−0.05(−0.05)	−0.09(−0.09)	−0.13(−0.13)	−0.18(−0.18)
9 $[Fe(CO)_5]$	−0.12	−0.02(−0.05)	−0.02(−0.02)	−0.02(−0.02)	−0.05(−0.05)	−0.07(−0.07)	−0.07(−0.06)
10 $[Fe(CO)_4]^{2-}$	−0.12	0.07(0.06)	0.07(0.06)	0.07(0.06)	0.03(0.02)	−0.01(−0.01)	0.01(0.01)
11 $[Fe(CN)_5NO]^{2-}$	−0.12	n.a.[b]	n.a.	n.a.	−0.16(−0.10)	−0.10(−0.10)	−0.16(−0.15)
12 $[FeO_4]^{2-}$	−0.67	−0.32(−0.34)	−0.32(−0.31)	−0.33(−0.31)	−0.44(−0.42)	−0.55(−0.52)	−0.82(−0.77)
MAE[c]		0.25(0.27)	0.25(0.26)	0.25(0.27)	0.24(0.25)	0.23(0.25)	0.25(0.26)
slope		0.43(0.39)	0.43(0.40)	0.42(0.39)	0.47(0.43)	0.52(0.48)	0.63(0.57)
intercept		0.07(0.05)	0.07(0.05)	0.07(0.07)	−0.02(−0.02)	−0.06(−0.07)	−0.13(−0.13)

[a] In parentheses, the results of nonrelativistic calculations. [b] See footnote *c* to Table 4. [c] Mean absolute error of the method. [d] See text for details of basis set. All shifts are given with respect to $[Fe(CN)_6]^{4-}$.

fraction of the HF exchange in one series of hybrid density functionals only.

Inclusion of the Hartee-Fock exchange in hybrid functionals leads to a certain increase in the systematic error as given by the intercept of the linear fit for both basis sets, A and B. At the same time, mixing in more HF exchange leads to an improved correlation of the calculated values with the experiment. The slope of the linear fit increases steadily as the fraction of the HF exchange increases. This effect is observed for both basis sets; however, the bigger basis set A provides better overall correlation with the experimental results. The hybrid functional BH&HLYP gives reasonable correlation with experiment and less systematic error compared to HF, for both basis sets A and B.

The improvement brought about by the inclusion of HF exchange in hybrid functionals warrants some discussion. In our opinion, the most plausible explanation for the inferior performance of pure density functionals is the incorrect behavior of the potential generated by such a functional near the nucleus. It is known that the gradient corrected functionals yield the Kohn−Sham potential which is divergent at the nuclear position.[41] Therefore, mixing in the HF exchange (the HF potential remains finite at the nucleus) cures partially this deficiency of pure density functionals and leads to improved results for the properties which critically depend on the electron distribution in the vicinity of the nucleus.

With the use of both basis sets, A and B, the difference between relativistic and nonrelativistic results is clearly visible. From all the parameters employed for the data analysis, it is evident that the inclusion of relativity leads to improved results as compared to the experiment. The difference between relativistic and nonrelativistic results is more pronounced for the large basis set A than for the small basis set B. This is understandable, because the basis set B was optimized and contracted in the nonrelativistic HF calculations and does not possess sufficient flexibility to accommodate changes in the electron distribution due to the inclusion of relativity. This underlines the necessity to develop compact basis sets adapted for the relativistic

Table 6. Comparison of Mossbauer Isomer Shifts (mm/s) from This Work (Using Basis Set B) with That of Ref 13, Recalculated According to the Current Method

	exptl	HF[a]	BH&HLYP[a]	B3LYP[a]	B3LYP[b]	BPW91[a]	BPW91[b]
1 $[Fe(H_2O)_6]^{2+}$	1.41	0.72	0.65	0.61	0.55	0.62	0.53
2 $[FeCl_4]^{2-}$	0.92	0.36	0.34	0.33	0.39	0.35	0.38
3 $[Fe(H_2O)_6]^{3+}$	0.52	0.21	0.23	0.24	0.18	0.31	0.21
4 $[FeF_6]^{3-}$	0.50	0.25	0.23	0.26	0.24	0.31	0.27
6 $[FeBr_4]^{1-}$	0.29	0.00	0.07	0.15	0.16	0.23	0.20
7 $[FeCl_4]^{1-}$	0.22	0.02	0.06	0.13	0.15	0.24	0.19
8 $[Fe(CN)_6]^{3-}$	−0.11	−0.18	−0.13	−0.09	−0.07	−0.05	−0.05
9 $[Fe(CO)_5]$	−0.12	−0.07	−0.07	−0.05	−0.05	−0.02	−0.05
10 $[Fe(CO)_4]^{2-}$	−0.12	0.01	−0.01	0.03	−0.08	0.07	−0.06
11 $[Fe(CN)_5NO]^{2-}$	−0.12	−0.16	−0.10	−0.16	−0.09	n.a.	−0.06
12 $[FeO_4]^{2-}$	−0.67	−0.82	−0.55	−0.44	−0.40	−0.32	−0.31
MAE[c]		0.25	0.23	0.24	0.24	0.25	0.24
slope		0.63	0.52	0.47	0.45	0.43	0.41
intercept		−0.13	−0.06	−0.02	−0.02	0.07	0.01

[α] This work. [b] Reference 13. [c] Mean absolute error of the method.

calculations. Nevertheless, the overall agreement with the experiment is acceptable for both hybrid functionals, B3LYP and BH&HLYP. Although the HF method provides the best correlation with the experimental results (slope of 0.78 and 0.63 with the basis sets A and B, respectively), the systematic error increases in the HF calculations as compared to pure or hybrid density functionals. In the overall assessment, the use of hybrid density functionals with an increased fraction of the HF exchange, such as the BH&HLYP functional, can be recommended for the calculation of MIS in iron complexes.

The computational procedure employed in the present work employs the proportionality constant a in eq 5 which was obtained from the experimentally measured parameters of nuclear transitions in ^{57}Fe. Therefore, its comparison with the results of the standard calculations of the MIS, where this constant is treated as an empirical parameter and is fitted against the experimental data, may be not straightforward. However, with the use of the contact densities published in ref 13, it is possible to calculate the MISs with the use of eq 5 and the nonempirical constant a. The so-obtained isomer shifts are compared in Table 6 with the shifts calculated with the use of eqs 3−5 in the present work. From this comparison, it is obvious that the standard approach does not have any numerical advantage before the method used in the present article, if the fitting procedure is excluded. In this sense, the method employed in this paper helps to make an unbiased judgment on the performance of the computational schemes used to calculate the MIS. Because it was not the purpose of the present work to obtain an empirically adjusted proportionality constant in eq 5, the use of a set of 12 molecules seems to be acceptable for making a reasonable judgment on the performance of different computational schemes. The use of the fitting procedure within the standard approach to MIS, although it leads to improved numerical results, does not allow for seeing the true accuracy of a selected quantum chemical method and may result in an unrealistic parameter of nuclear γ-transitions as obtained from the fitted proportionality constant a in eq 5. It is our goal to avoid the empirical fitting and to find out computational schemes capable of yielding accurate results from first principles.

IV. Conclusion

In the present work, a recently developed approach to the theoretical calculation of Mössbauer isomer shift[20] is applied within the context of density functional theory. Within the new approach, the MIS is calculated as a derivative of the electronic energy with respect to the radius of the finite nucleus.[20] Note that no empirical parameters are employed in the new approach, and the calibration of the parameters which connect the theoretical electron density at the nucleus with the experimental values of MIS is thus avoided. Therefore, the new approach offers a possibility to carry out an unbiased comparison of different computational methods applied to the MIS calculation. Furthermore, the present method has the advantage that it can be used with any quantum chemical computational scheme regardless of the availability of the relaxed density matrix within this scheme.

In the present work, we carried out calculations of MIS for a series of iron complexes. The computational schemes employed include both hybrid and pure density functionals as well as the HF method. Before the performance of density functional methods was addressed, the dependence of the quality of the calculated MIS on the size of the basis set was studied.

The investigation of the effect of the basis set truncation within the context of the new approach reveals that the MISs are not very sensitive to the removal/addition of the tightest primitive functions from/to a large uncontracted basis set. Therefore, for obtaining converged theoretical values, it is sufficient to employ only one tight s-type primitive function added to the standard uncontracted basis set (see the basis set A). With the use of the small contracted basis set (see the basis set B), an acceptable accuracy in the calculated MIS is obtained for the HF and density functional methods. The use of the small basis set, such as the basis set B, is therefore a reasonable compromise between accuracy and complexity of the calculation.

The investigation of the performance of different density functionals reveals that the pure density functional methods

provide poorer correlation of the calculated MIS with the experimental values. Irrespective of the size of the basis set employed, the hybrid functionals provide a consistently better description of the MIS. Correlation of the calculated MIS with the experimental values improves with the increasing fraction of the HF exchange, however at a price of somewhat greater systematic error. In the overall assessment, the hybrid functionals with a greater fraction of the HF exchange such as the BH&HLYP functional produce a better description of the MIS in iron complexes.

Generally, the density functional methods demonstrate somewhat inferior numeric accuracy as compared to the ab initio wave function methods. A tenable explanation for this is in the incorrect behavior of modern approximate density functionals (and respective potentials) near the nucleus.[41] Mixing in the HF exchange energy partially corrects this deficiency. However, quite a substantial fraction of the HF exchange is needed to achieve a noticeable improvement. It appears that a more universal solution would be to switch to the orbital dependent density functionals which are capable of the exact treatment of a substantial portion of the exchange-correlation energy.

References

(1) Mössbauer, R. L. *Z. Phys.* **1958**, *151*, 124.

(2) Gütlich, P.; Link, R.; Trautwein, A. In *Mössbauer Spectroscopy and Transition Metal Chemistry*; Springer: New York, 1978.

(3) (a) Shenoy, G. K.; Dulap B. D. In *Mössbauer Isomer Shifts*; Shenoy, G. K., Wagner, F. E., Eds.; North-Holland: Amsterdam 1978; pp 869−894. (b) Shenoy, G. K.; Dulap B. D. In *Mössbauer Isomer Shifts*; Shenoy, G. K., Wagner, F. E., Eds.; North-Holland: Amsterdam 1978; pp 17−48.

(4) Kagan, Yu. M.; Lyubutin, I. S. In *Applications of the Mössbauer effect*; Gordon & Breach: New York, 1985; Vol. 4.

(5) Gütlich, P.; Ensling, J. In *Inorganic Electronic Structure and Spectroscopy*; Solomon, E. I., Lever, A. B. P., Eds.; John Wiley and Sons: New York, 1999; Vol. 1, pp 161−212.

(6) (a) Münck, E. In *Physical Methods in Bioinorganic Chemistry: Spectroscopy and Magnetism*; Que, L., Jr., Ed.; University Science Books: Sausalito, 2000; p 287. (b) Münck, E.; Stubna, A. In *Comprehensive Coordination Chemistry II;* Lever, A. B. P., Ed.; Elsevier: New York, 2002; Vol. 2.

(7) Mørup, S. *Mössbauer Effect Ref. Data J.* **2002**, *25*, 105.

(8) Kistner, O. C.; Sunyar, A. W. *Phys. Rev. Lett.* **1960**, *4*, 412−415.

(9) Shirley, D. A. *Rev. Mod. Phys.* **1964**, *36*, 339−351.

(10) de Vries, J. L. K. F.; Trooster, J. M.; Ros, P. *J. Chem. Phys.* **1975**, *63*, 5256−5262.

(11) Trautwein, A.; Harris, F. E.; Freeman, A. J.; Descaux, J. P. *Phys. Rev. B* **1975**, *11*, 4101−4105.

(12) Neese, F. *Inorg. Chim. Acta* **2002**, *337*, 181−192.

(13) Nemykin, V. N.; Hadt, R. G. *Inorg. Chem.* **2006**, *45*, 8297−8307.

(14) Nieuwpoort, W. C.; Post, D.; van Duijnen, P. Th. *Phys. Rev. B* **1978**, *17*, 91−98.

(15) Lovell, T.; Li, J.; Liu, T.; Case, D. A.; Noodelman, L. *J. Am. Chem. Soc.* **2001**, *123*, 12392−12410.

(16) Lovell, T.; Han, W. G.; Liu, T.; Noodelman, L. *J. Am. Chem. Soc.* **2002**, *124*, 5890−5894.

(17) Svane, A.; Christensen, N. E.; Rodriguez, C. O.; Methfessel, M. *Phys. Rev. B* **1997**, *55*, 12572−12577.

(18) Sinnecker, S.; Slep, L. D.; Bill, E.; Neese, F. *Inorg. Chem.* **2005**, *44*, 2245−2254.

(19) (a) Bartlett, R. J. In *Geometrical Derivatives of Energy Surfaces and Molecular Properties*; Jørgensen, P., Simons, J., Eds.; Reidel: Dordrecht, 1986. (b) Gauss, J.; Cremer, D. *Adv. Quantum Chem.* **1992**, *23*, 205.

(20) Filatov, M. *J. Chem. Phys.* **2007**, *127*, 084101.

(21) Visscher, L.; Dyall, K. G. *At. Data Nuc. Data Tables* **1997**, *67*, 207.

(22) Kraka, E.; Gräfenstein, J.; Filatov, M.; Polo, V.; Wu, A.; He, Y.; Olsson, L.; Konkoli, Z.; He, Z.; Gauss, J.; Reichel, F.; Cremer, D. *COLOGNE 2005*; Göteborg University: Göteborg, 2005.

(23) (a) Dyall, K. G. *J. Chem. Phys.* **2001**, *115*, 9136−9143. (b) Dyall, K. G. *J. Comput. Chem.* **2002**, *23*, 786−793.

(24) Dyall, K. G. *J. Chem. Phys.* **1997**, *106*, 9618−9626.

(25) Filatov, M.; Dyall, K. G. *Theor. Chem. Acc.* **2007**, *117*, 333−338.

(26) Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* **1996**, *77*, 3865−3868.

(27) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098−3100.

(28) (a) Perdew, J. P.; Wang, Y. *Phys. Rev. B* **1992**, *45*, 13244−13249. (b) Perdew, J. P.; Burke, K.; Wang, Y. *Phys. Rev. B* **1996**, *54*, 16533−16539.

(29) (a) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785−789. (b) Miehlich, B.; Savin, A.; Stoll, H.; Preuss, H. *Chem. Phys. Lett.* **1989**, *157*, 200−206.

(30) Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J. *J. Phys. Chem.* **1994**, *98*, 11623−11627.

(31) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 1372−1377.

(32) Visser, O.; Aerts, P. J. C.; Hegarty, D.; Nieuwpoort, W. C. *Chem. Phys. Lett.* **1987**, *134*, 34−38.

(33) Kerler, W.; Neuwirth, W.; Fluck, E. *Z. Phys.* **1963**, *175*, 200−220.

(34) Patridge, H. *J. Chem. Phys.* **1987**, *87*, 6643−6647.

(35) Ahlrichs, R.; May, K. *Phys. Chem. Chem. Phys.* **2000**, *2*, 943.

(36) Dunning, T. H., Jr. *J. Chem. Phys.* **1989**, *90*, 1007−1023.

(37) Glukhovstev, M. N.; Pross, A.; McGrath, M. P.; Radom, L. *J. Chem. Phys.* **1995**, *103*, 1878−1885.

(38) (a) Wachters, A. J. H. *J. Chem. Phys.* **1970**, *52*, 1033−1036. (b) Wachters, A. J. H. In *IBM Tech. Rept. RJ584*; 1969. (c) Bauschlicher, C. W.; Langhoff, S. R., Jr.; Barnes, L. A. *J. Chem. Phys.* **1989**, *91*, 2399−2411.

(39) (a) Petersson, G. A.; Al-Laham, M. A. *J. Chem. Phys.* **1991**, *94*, 6081−6090. (b) Petersson, G. A.; Bennett, A.; Tensfeldt, T. G.; Al-Laham, M. A.; Shirley, W. A.; Mantzaris, J. *J. Chem. Phys.* **1988**, *89*, 2193−2218.

(40) Godbout, N.; Salahub, D. R.; Andzelm, J.; Wimmer, E. *Can. J. Chem.* **1992**, *70*, 560−571.

(41) van Leeuwen, R.; Baerends, E. J. *Phys. Rev. A* **1994**, *49*, 2421−2431.

(42) Friedt, J. M.; Petridis, D.; Sanchez, J. P.; Reschke, R.; Trautwein, A. *Phys. Rev. B* **1979**, *19*, 360−364.

(43) Wertheim, G. K.; Herber, R. H. *J. Chem. Phys.* **1962**, *36*, 2497−2499.

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